

# Search for spin gapless semiconductors: The case of inverse Heusler compounds

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We employ *ab-initio* electronic structure calculations to search for spin gapless semiconductors, a recently identified new class of materials, among the inverse Heusler compounds. The occurrence of this property is not accompanied by a general rule and results are materials specific. The six compounds identified show semiconducting behavior concerning the spin-down band structure and in the spin-up band structure the valence and conduction bands touch each other leading to 100% spin-polarized carriers. Moreover these six compounds should exhibit also high Curie temperatures and thus are suitable for spintronics applications.

The rapid growth of nanotechnology the last two decades brought to the attention of scientific research novel materials with novel properties. Especially the design of new magnetic nanomaterials leded the development of spintronics.<sup>1</sup> To achieve the incorporation of spin in electronic devices there are two ways: either the development of magnetic materials at the nanoscale, e.g. the growth of half-metallic ferromagnetic Heusler compounds,<sup>2</sup> or the doping of semiconductors with magnetic ions like in diluted magnetic semiconductors.<sup>3</sup> All these developments were triggered by the development of computational materials science, which made accessible the simulation of compounds in order to predict the electronic, magnetic, optical,... properties. Moreover simulations allow to study known alloys in new metastable structures where their properties are completely altered with respect to the known stable lattice structures.

A special class of materials incorporated the so-called gapless semiconductors; semiconductors with vanishing gap width.<sup>4</sup> These materials are of special interest since the mobility of carriers is considerably larger than usual semiconductors. The first gapless semiconductors studied were Hg-based IV-VI compounds, such as HgCdTe, HgCdSe and HgZnSe, but these alloys are toxic and easily oxidized.<sup>4</sup> Afterwards, PbPdO<sub>2</sub> was proposed to be a gapless semiconductor,<sup>5</sup> and the zero gap-width was also demonstrated experimentally.<sup>6</sup> The most known gapless semiconductor is the graphene.<sup>7</sup> Wang in 2008 proposed that the doping of PbPdO<sub>2</sub> would lead to a new class of materials which he named spin gapless semiconductors (SGS).<sup>8</sup> SGS is the border between half-metallic (HM) ferromagnets<sup>9</sup> and semiconductors and a schematic representation of the density of states (DOS) is shown in Fig.1. In a half-metallic ferromagnet the spin-up (majority-spin) band is crossed by the Fermi level as in a usual magnetic metal while in the spin-down (minority-spin) band a gap exists and the Fermi level falls within

the gap as in semiconductors. In the case of SGS the picture of the spin-down band is similar to the HM but now in the spin-up band the Fermi level falls within a zero-width gap. The system can be still magnetic since the two spin-band structures are different. The advantage of SGS is that no-energy is required to excite electrons from the valence to the conduction band, and excited carriers (both electrons and holes) can be 100% spin-polarized simultaneously leading to new functionalities of spintronics devices. Other SGS materials include (i) the graphene ribbons altered by CH<sub>2</sub> radical groups,<sup>10</sup> where the magnetism stems from the unsaturated carbon states, (ii) the ferromagnetic semiconductor HgCr<sub>2</sub>Se<sub>4</sub> which becomes SGS under a pressure of 9 GPa,<sup>11</sup> and (iii) the BN nanoribbons with vacancies.<sup>12</sup>

Heusler compounds is a huge family of compounds with more than 1000 members exhibiting a variety of diverse magnetic phenomena.<sup>13</sup> Almost all compounds crystallize in a cubic close-packed structure similar to the zinc-blende structure of binary semiconductors. Recently, new phenomena have been identified in some of these Heusler groups like topological insulators,<sup>14</sup> half-metallic ferromagnets,<sup>9,15</sup> half-metallic antiferromagnets,<sup>16–18</sup> multifunctional Heuslers for recording,<sup>19</sup> etc. Thus one could easily imagine the possibility of finding also Heusler compounds being SGS among them. It seems that this is true among the so-called inverse full-Heusler compounds of the X<sub>2</sub>YZ chemical formula crystallizing in the so-called XA structure with space group  $F\bar{4}3m$ ; the prototype being CuHg<sub>2</sub>Ti. The lattice is actually a fcc one with four atoms as basis along the diagonal occupied in the sequence X-X-Y-Z. X and Y are transition metal atoms and for the XA structure to occur the valence of X should be lower than the valence of Y. Examples are Cr<sub>2</sub>MnSb,<sup>20</sup> Mn<sub>2</sub>CoGa,<sup>21</sup> Cr<sub>2</sub>CoGa,<sup>17</sup> etc. Recently, Ouardi and collaborators identified Mn<sub>2</sub>CoAl to be a SGS and experimental evidence was given towards this direction.<sup>22</sup> Heusler compounds compared to other potential SGSs have the advantage of being compatible with current semiconductors technology, their magnetic properties are stable and

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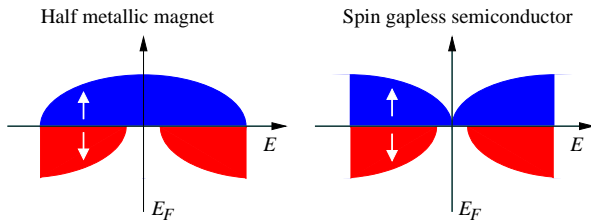


FIG. 1. (Color online) Schematic representation of the density of states of a half-metallic system (left panel) and of a spin gapless semiconductor (right panel). With blue (red) we show the spin-up (spin-down) states.

there is a continuously growing knowhow on the synthesis of such alloys in the form of films.<sup>13</sup> In this Letter we have used the full-potential nonorthogonal local-orbital minimum-basis band structure scheme (FPLO)<sup>23</sup> within the generalized gradient approximation (GGA)<sup>24</sup> to study the electronic and magnetic properties of all the inverse  $X_2YZ$  alloys where  $X=\text{Sc, Ti, V, Cr or Mn}$ ,  $Y=\text{Al, Si or As}$  and  $Z$  is a transition-metal atom ranging from Ti to Zn. First we determined the equilibrium lattice constants using total energy calculations and a dense  $20\times 20\times 20$   $\mathbf{k}$ -point grid to carry out the numerical integrations. Our results have shown that within this large number of Heuslers studied there are six of them being SGS:  $\text{Ti}_2\text{MnAl}$ ,  $\text{Ti}_2\text{CoSi}$ ,  $\text{Ti}_2\text{VAs}$ ,  $\text{V}_3\text{Al}$ ,  $\text{Cr}_2\text{ZnSi}$  and  $\text{Mn}_2\text{CoAl}$ . The present Letter focuses on these six alloys which can be incorporated as SGS in spintronics devices.

As we just mentioned we have identified six inverse Heusler compounds which are SGSs and in Table I, we have gathered the calculated equilibrium lattice constants and magnetic moments. First, to calculate the equilibrium lattice constants we have performed total energy calculations scanning a wide range of lattice constant values and taking a more dense grid around the one minimizing the total energy. Then we have fitted a quadratic polynomial using the values close to the energy minimum in order to better estimate it. The use of GGA is crucial since the local-spin-density-approximation (LSDA) is well-known to underestimate the equilibrium lattice constants with respect to experimental values. The calculated values, as shown in Table I exceed the 6 Å for the Ti-based alloys and  $\text{V}_3\text{Al}$  while they are considerably smaller for  $\text{Cr}_2\text{ZnSi}$  and  $\text{Mn}_2\text{CoAl}$ . This is expected since Ti and V atoms have large atomic radius and their  $d$ -wavefunctions extend more in space with respect to Cr and Mn atoms. Between the two latter compounds  $\text{Cr}_2\text{ZnSi}$  has the larger equilibrium lattice constant due to the presence of the larger Zn atom with respect to the Co one in  $\text{Mn}_2\text{CoAl}$ . The experiments by Ouardi *et al.* on  $\text{Mn}_2\text{CoAl}$  gave a lattice constant of 5.798 Å,<sup>22</sup> which deviates less than 1.2% from our estimated values of 5.73 Å.

Also in Table I, we present the atom-resolved spin magnetic moments in  $\mu_B$  and the total one per formula unit

TABLE I. Calculated equilibrium lattice constant and spin magnetic moments in  $\mu_B$  for the inverse Heusler compounds under study. We use the symbols A and B to denote the two early transition metal atoms sitting at different sites (see text for explanation). Note that the total spin magnetic moment is given per formula unit (which coincides with the per unit cell value). The last column is the sum of the absolute values of the atom-resolved spin magnetic moments.

$X_2YZ$	$a(\text{\AA})$	$m^{X(A)}$	$m^{X(B)}$	$m^Y$	$m^Z$	$m^{total}$	$m^{abs}$
$\text{Ti}_2\text{MnAl}$	6.24	1.44	1.30	-2.74	-0.01	0	5.49
$\text{Ti}_2\text{CoSi}$	6.03	1.80	0.86	0.35	-0.02	3	3.03
$\text{Ti}_2\text{VAs}$	6.23	1.31	0.53	-1.86	0.01	0	3.71
$\text{V}_3\text{Al}$	6.09	1.64	0.00	-1.64	0.00	0	3.28
$\text{Cr}_2\text{ZnSi}$	5.85	-1.89	1.93	0.01	-0.05	0	3.88
$\text{Mn}_2\text{CoAl}$	5.73	-1.65	2.80	0.94	-0.08	2	5.47

which for these compounds coincides with the per unit cell value. We use the superscripts A and B to distinguish the two X atoms sitting at the A and B sites (for the structure see Ref. 20). We should first comment on the total spin magnetic moments. For all compounds the obtained values are integers. This is expected since due to the gaps the total number of occupied states in both spin directions is integer and thus the difference between the spin-up and spin-down occupied states, which equals to the total spin magnetic moment in  $\mu_B$ , is also an integer. The four alloys  $\text{Ti}_2\text{MnAl}$ ,  $\text{Ti}_2\text{VAs}$ ,  $\text{V}_3\text{Al}$  and  $\text{Cr}_2\text{ZnSi}$  exhibit a zero total spin magnetic moment and thus can be also classified as half-metallic antiferromagnets also known as half-metallic fully-compensated ferrimagnets.<sup>17</sup> The other two compounds,  $\text{Ti}_2\text{CoSi}$  and  $\text{Mn}_2\text{CoAl}$ , show a net total spin magnetic moment of 3 and  $2 \mu_B$  respectively. This behavior of the total spin magnetic moment follows a generalized version of the Slater-Pauling behavior of the Heusler compounds<sup>25,26</sup> and will be discussed elsewhere.<sup>27</sup> The advantage of the half-metallic antiferromagnetic compounds is that they create no external fields and thus lead to minimal energy losses.

The atom resolved spin moments do not show a coherent behavior among all compounds. To understand their behavior we have to take into account the so-called Bethe-Slater curve.<sup>28</sup> The Cr and Mn atoms when nearest neighbors tend to couple antiferromagnetically and this explains the relative orientation of the spin magnetic moments for  $\text{Cr}_2\text{ZnSi}$  and  $\text{Mn}_2\text{CoAl}$  presented in Table I. The Zn atom has all its  $d$ -states filled and only the delocalized  $4s$  electrons contribute to magnetism leading to a negligible Zn spin magnetic moment in  $\text{Cr}_2\text{ZnSi}$ . Co couples ferromagnetically to its nearest-neighboring Mn<sup>B</sup> atom due to the hybridization of the  $d$ - $d$  orbital as occurs also in the usual full-Heusler compounds containing Co and Mn.<sup>26</sup> In the case of the Ti-based compounds the two Ti atoms have parallel spin magnetic moments as expected by the Bethe-Slater curve. The spin moments of Mn and V atoms are antiparallel to the spin moments of the Ti atoms while the spin moment of the Co atom is ferromagnetically coupled to the one of the Ti atoms

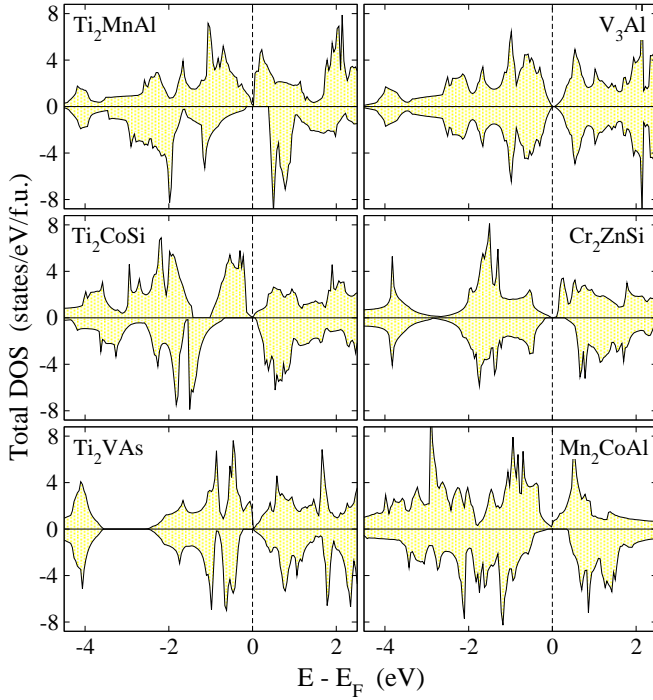


FIG. 2. (color online) Total density of states (DOS) per formula unit for the compounds under study. Positive DOS values correspond to the majority-spin (spin-up) states and negative DOS values to the minority-spin (spin-down) states. The zero of the energy axis corresponds to the Fermi level.

in  $\text{Ti}_2\text{CoSi}$  compound.  $\text{V}_3\text{Al}$  is a special case since the V atoms at the A and C sites have antiparallel spin magnetic moments of the same magnitude while the V atom at the B site and the As atom have no net spin magnetic moment. The two V atoms at the A and C sites are equivalent by symmetry,<sup>26</sup> and thus are only allowed to have either parallel or antiparallel spin magnetic moments of the same magnitude. The second configuration is the ground state as our total energy calculations suggest. By symmetry the V atoms at the B site has as nearest neighbors eight V atoms, four at the A site and four at the C site, and thus by symmetry should have a zero spin magnetic moment. The *sp* atoms at the Z sites have very small spin magnetic moments in all cases. The experiments of Ouardi et al in Ref. 22 gave for  $\text{Mn}_2\text{CoAl}$  a total spin magnetic moment of  $2 \mu_B$  as predicted by our calculations, while their first-principles calculations gave for the atom-resolved spin magnetic moments about -2, 3 and  $1 \mu_B$  for the  $\text{Mn}^A$ ,  $\text{Mn}^B$  and Co atoms in agreement with our results.

Now let us discuss the main finding of our study: the appearance of spin gapless semiconducting behavior in these six compounds. In Fig. 2 we present the total density of states (DOS) for all six compounds. Positive DOS values concern the majority-spin or spin-up states and negative DOS values the minority-spin or spin-down states (in the case of zero total spin magnetic moments the terms majority-spin and minority spin are meaning-

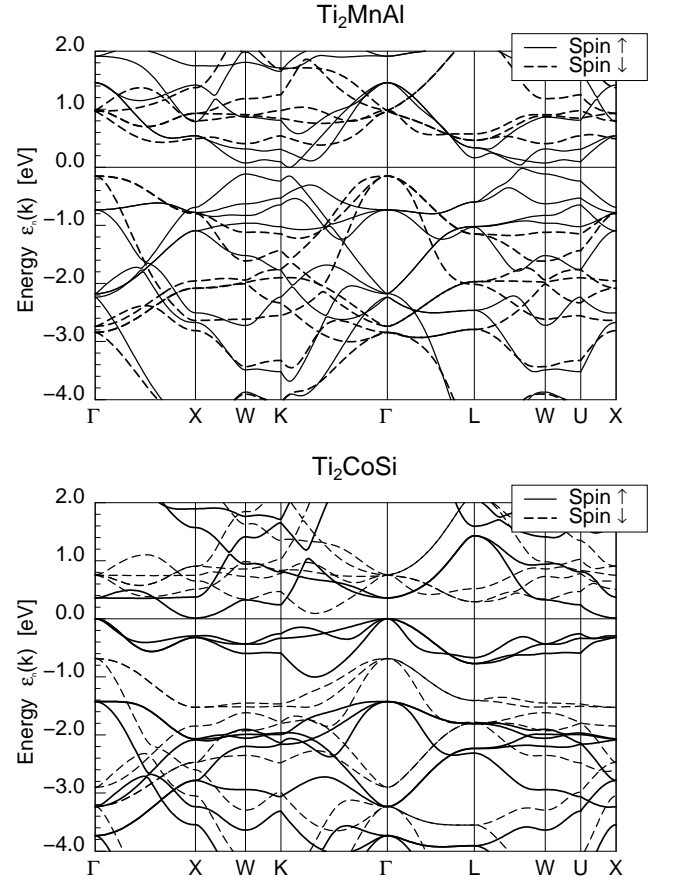


FIG. 3. Band structure along the high-symmetry directions for the  $\text{Ti}_2\text{MnAl}$  (upper panel) and  $\text{Ti}_2\text{CoSi}$  (lower panel) compounds. The zero energy value in the vertical axis corresponds to the Fermi energy. With the solid [dashed] lines we present the majority-spin (spin-up) [minority-spin (spin-down)] electronic bands.

less). In all six cases there is a sizeable gap in the spin down band structure and the Fermi level falls within this gap. In the spin-up band structure the valence and conduction bands touch each other and the Fermi level falls within a zero-width gap. Thus these compounds can be classified as SGSs. The width of the spin-down gap is larger for  $\text{Ti}_2\text{CoSi}$  which has the highest total spin magnetic moment of  $3 \mu_B$ , since in that case the exchange splitting between the two spin bands is expected to be strong. Although the total spin magnetic moment for  $\text{Mn}_2\text{CoAl}$  is also important, the antiferromagnetic coupling of the neighboring spin-magnetic moments leads to a spin-down gap comparable to the other half-metallic antiferromagnetic compounds.  $\text{V}_3\text{Al}$  is a special case since the spin-down and spin-up bands are identical. If we examine the states close to the spin-up gap we can see that they do not have the same behavior in all cases, *e.g.* in  $\text{Ti}_2\text{MnAl}$  they are more steep than in  $\text{Cr}_2\text{ZnSi}$ .

The question which arises is if there is a common feature in the band structure of these compounds which could lead to an on-demand design of these materials. We have plotted the spin-dependent band structure for

all six compounds. The  $\text{Mn}_2\text{CoAl}$  band structure is similar to the one calculated in Ref. 22 with a  $\Gamma$ -X indirect gap in the spin-up band. In Fig. 3 we show the band-structure for  $\text{Ti}_2\text{MnAl}$  and  $\text{Ti}_2\text{CoSi}$  focusing around the Fermi level. In the case of  $\text{Ti}_2\text{MnAl}$  we have a direct gap in the midpoint between the L and W high-symmetry points. In the case of  $\text{Ti}_2\text{CoSi}$  we have an indirect gap with the maximum of the valence spin-up states at the  $\Gamma$  point and the minimum of the conduction spin-up states at the X-point like for  $\text{Mn}_2\text{CoAl}$ . Overall the band structures are quite different and no safe conclusion can be drawn. Also in the case of  $\text{Mn}_2\text{CoAl}$  if we replace Ga or In for Al, which belong to the same column of the periodical table, the  $\text{Mn}_2\text{CoGa}$  and  $\text{Mn}_2\text{CoIn}$  alloys are no more SGS and are simple half-metallic ferrimagnets.<sup>29</sup> It seems that the appearance of a zero gap in the spin-up band structure is a rare phenomenon which is material dependent and no general rules exist concerning the design of new SGSs.

Finally, we would like to comment on the expected Curie temperature,  $T_C$ , of these compounds which is crucial for applications. Previous extensive studies on multi-sublattice half-metallic Heusler compounds have shown that the Curie temperature is more or less proportional to the total spin magnetic moment (or sum of the absolute values of the atomic spin magnetic moments in the case of ferrimagnets) since the  $T_C$  is mainly determined by nearest neighbor inter-sublattice exchange interactions.<sup>17,30,31</sup> Among the considered compounds  $\text{Mn}_2\text{CoAl}$  was found experimentally to have a Curie temperature of 720 K in Ref. 22 while the sum of the absolute values of the spin moments (see last column of Table I) is  $5.47 \mu_B$ . Based on this empirical rule we expect a  $T_C$  of 400 K for  $\text{Ti}_2\text{CoSi}$  which has the lowest sum. An interesting case is  $\text{Ti}_2\text{MnAl}$  which combines a zero total spin moment with a very high Curie temperature as expected from the very large sum of the absolute values of the atomic spin moments which is almost identical to  $\text{Mn}_2\text{CoAl}$ .

Employing *ab-initio* electronic structure calculation, we have identified six spin gapless semiconductors among the inverse Heusler compounds:  $\text{Ti}_2\text{MnAl}$ ,  $\text{Ti}_2\text{CoSi}$ ,  $\text{Ti}_2\text{VAs}$ ,  $\text{V}_3\text{Al}$ ,  $\text{Cr}_2\text{ZnSi}$  and  $\text{Mn}_2\text{CoAl}$ . All six compounds show a semiconducting behavior in the spin-down band while in the spin-up band structure the valence and conduction bands touch each other. No general rule can be stated to predict the occurrence of this property. The behavior of the spin magnetic moments can be explained based on the Bethe-Slater curve. Moreover, we expect these alloys to exhibit Curie temperatures exceeding the room temperature and thus they are suitable for spintronics applications since both type of carriers, electrons and holes, are spin-polarized and can be separately manipulated. We expect the results in this Letter to trigger further experimental research, as in Ref. 22 towards the growth of such nanostructures.

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